

## CLAIMS

(63)

1. A method of dry cleaning an article, especially fabric, comprising the successive steps of:
- 5 a) contacting the article with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa, so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and
- b) separating the article and the fluid dry cleaning composition;
- 10 wherein the fluid dry cleaning composition comprises ionic surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in an undissolved solid form; said ionic surfactant being represented by the formula  $R_1X$ ,  $XR_1X$  or  $R_2YR_2$ ; wherein:
- 15  $R_1$  is a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkyl; a substituted or unsubstituted, optionally heterogeneous  $C_3$ - $C_{16}$  cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;
- $R_2$  and  $R_2$  independently are  $R_1$ ,  $X$ ,  $R_aX$  or  $R_a(X)_2$ ;
- $R_a$  is a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkyl;
- 20 a substituted or unsubstituted, optionally heterogeneous  $C_3$ - $C_{16}$  cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;
- and wherein
- $X$  is  $NH_2$ ,  $NH_3^+$ ,  $COOM_1$ ,  $COO^-$ ,  $OP(O)(OM_1)(OM_2)$ ,  $OS(O)_2(OM_1)$ ;
- 25  $Y$  is  $NH$ ; and
- $M_1$  and  $M_2$  independently represent sodium, potassium, ammonium or hydrogen.
2. The method according to claim 1, wherein the duration of step a) exceeds 1 minute, preferably 2 minutes.
- 30 ~~3. The method according to claim 1 or 2, wherein the ionic surfactant contains one or more lipophilic hydrocarbon residues with 3-25 carbon atoms and one or more groups selected from amine, phosphate, phosphonate, phosphinate, phosphonite, phosphine, phosphinite, phosphite,~~

quaternary phosphonium salt, quaternary ammonium salt, sulphate, sulphonate, sulphinate, sulphenate, sulphide and carboxylate groups.

4. The method according to any one of claims 1-3, wherein the ionic surfactant is represented by the formula  $R_1X$ ,  $XR_1X$ ,  $R_2YR_2$ ,  $R_3Z(R_3)R_3$  or  $R_3E(R_3)(R_3)R_3D$ ; wherein:
- $R_1$  is a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkyl; a substituted or unsubstituted, optionally heterogeneous  $C_3$ - $C_{16}$  cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;
- $R_2$  and  $R_2$  independently are  $R_1$ ,  $X$ ,  $R_aX$  or  $R_a(X)_2$ ;
- $R_3$ ,  $R_3$ ,  $R_3$  and  $R_3$  independently are  $R_1$ ,  $X$ ,  $R_aX$ ,  $YR_1$ ,  $R_a(YR_a)_nYR_1$  or  $Y(R_aY)_nR_1$ ;
- $R_a$  is a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkyl; a substituted or unsubstituted, optionally heterogeneous  $C_3$ - $C_{16}$  cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_1$ - $C_{22}$  alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;
- and wherein
- $X$  is  $NH_2$ ,  $NH_3^+$ ,  $OP(O)(OM_1)(OM_2)$ ,  $OP(O)_3^{2-}Q^{2+}$ ,  $P(O)(OM_1)(OM_2)$ ,  $P(O)_3^{2-}Q^{2+}$ ,  $P(O)(H)(OM_1)$ ,  $OS(O)_2(OM_1)$ ,  $S(O)_2(OM_1)$ ,  $S(O)(OM_1)$ ,  $COO^-$  or  $COOM_1$ ;
- $Y$  is  $NH_2$ ,  $NH_3^+$ ,  $OP(O)(OM_1)O$ ,  $P(O)(OM_1)O$ ,  $P(O)(OM_1)$ ,  $OS(O)_2O$ ,  $S(O)_2O$ ,  $S(O)O$ ;
- $Z$  is  $N$ ,  $NH^+$ ;
- $E$  is  $N^+$ ;
- $D$  is  $F^-$ ,  $Cl^-$ ,  $Br^-$  or  $I^-$ ;
- $M_1$  and  $M_2$  independently represent sodium, potassium, ammonium or hydrogen;
- $Q^{2+}$  represents  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Mg^{2+}$  or  $Zn^{2+}$ ; and
- $n=0-20$ .

3. The method according to claim 1 or 2, wherein the method comprises a rinsing step wherein the fluid dry cleaning composition is replaced by a rinsing composition containing densified carbon dioxide, but no undissolved ionic surfactant.
4. The method according to claim 3, wherein the rinsing composition contains co-solvent and/or water.

5. The method according to claim 4, wherein  $X$  is  $NH_2$  and/or  $COOM_1$  and  $Y$  is  $NH$ , the ionic surfactant is represented by the formula  $R_1X$ ,  $XR_1X$ , or  $R_2YR_2$ , wherein  $X$  is  $NH_2$ ,  $NH_3^+$ ,  $COOM_1$ ,  $COO^-$ ,  $OP(O)(OM_1)(OM_2)$ ,  $OS(O)_2(OM_1)$  and  $Y$  is  $NH$ .
6. The method according to claim 4, wherein  $R_1$  and  $R_a$  independently are a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_3$ - $C_{22}$  alkyl or are a substituted or unsubstituted, linear or branched, optionally heterogeneous  $C_3$ - $C_{22}$  alkenyl.
7. The method according to any one of claims 1-6, wherein the fluid dry cleaning composition contains between 0.0001 and 5 wt.% water.
8. The method according to any one of claims 1-7, wherein the fluid dry cleaning composition contains a co-solvent selected from the group consisting of aliphatic and aromatic hydrocarbons, and esters and ethers thereof, alkyl and dialkyl carbonates, alkylene and polyalkylene glycols, and ethers and esters thereof, lactones, alcohols and diols, polydimethylsiloxanes and combinations thereof..
9. The method according to any one of claims 1-8, wherein step a) comprises contacting the article with the fluid dry cleaning composition at a temperature between 0 and 30°C.
10. The method according to any one of claims 1-10, wherein step a) comprises contacting the article with the fluid dry cleaning composition at a pressure between 2 and 25 MPa.